

REVIEW

Near infrared reflectance spectroscopy for online particle size analysis of powders and ground materials^a

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The cross-sensitivity of near infrared (NIR) reflectance to the particle size of powders or ground materials has long been documented but not fully exploited for particle size estimation. Diffuse reflectance of a powder sample is dependent on light scattering within its layers, and a powder's absorption and scattering coefficient are related to its particle size. This is the basis of NIR reflectance–particle size calibrations. The availability of fibre optic probes and the speed of NIR spectrometers make them suitable for remote and online sensing of particle size, in addition to providing chemical information of a powder sample. The basics of NIR reflectance spectroscopy relevant to particle size determination and its relation to sample preparations, methods of presentation, reference methods, calibration development and validation are reviewed in this paper.

Keywords: near infrared, NIR, spectroscopy, reflectance, particle size, powders

Introduction

Near infrared (NIR) spectroscopy extracts usable information from the absorption spectral character-

istics of a sample irradiated by light in the NIR region.¹ The NIR region (780–2500 nm) is dominated by overtone and combination bands of fundamental vibrations occurring in the mid-infrared.

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It has long been recognised that NIR reflectance is sensitive to the particle size, shape and distribution of powders or granular samples.^{2–7} A sensor that has sensitivity to two measurable quantities is said to exhibit cross-sensitivity. For these sensors, calibration involves maximising the wanted and minimising the unwanted signal. For conventional NIR reflectance applications, i.e. determining chemical compounds in granular or powdered samples, particle size effects on the spectra is considered the unwanted signal, or noise. Therefore, to ensure adequate precision in quantitative chemical analyses, particle size effects are reduced by grinding the sample finely to a near-uniform size followed by proper sampling^{8,9} or by correcting the spectra using derivatives, multiple scattering correction, standard normal variate and detrending, and special transformations.^{6,10–12}

Conversely, the cross-sensitivity of NIR reflectance can be exploited for particle size analysis. Due to its proven reliability and speed in multi-constituent monitoring and control^{13,14} and the availability of fibre optic probes, NIR reflectance is receiving renewed interest as a potential online sensor for particle size.^{15–17} Because only one sensor is needed to monitor both chemical constituents and particle size,^{15,18} NIR reflectance has advantages in powder analysis over other methods. Recently, it has been successfully used for online monitoring of powder blending.^{19,20} This review aims to integrate the basics of NIR reflectance spectroscopy relevant to particle size analysis of powders and ground materials and relate these with the sample preparations, methods of sample presentation and calibration techniques for developing and validating NIR reflectance–particle size models, with emphasis on potential online applications.

Theory

Classical absorption spectroscopy has its foundation in Beer–Lambert’s law, which states that for a homogenous and non-scattering liquid sample, the concentration of an absorber is directly proportional to the sample absorbance. In NIR diffuse reflectance spectroscopy, the requirements of classical absorption spectroscopy are not completely satisfied be-

cause the sample is non-homogenous and scattering.²¹ The path length of light for absorption spectroscopy is constant, whereas for reflectance spectroscopy path length is a function of the microscopic structure of the material containing the absorber.²² The theory of NIR reflectance spectroscopy is not fully defined, but empirical results show that Beer–Lambert’s law holds, at least in principle.²¹

An NIR beam incident on a powdery or granular material of a weakly-absorbing medium, thick enough to prevent transmission (effectively infinite), will penetrate the layer and its direction will be changed each time a particle boundary is encountered. The changes in direction are a result of reflection, refraction and random diffraction at the surfaces of various particles. The combination of these effects is called light scattering.²² Light propagates through a diffusely reflecting material through scattering. As scattered light encounters more boundaries of particles, further scattering occurs in all directions and part of it is absorbed, which diminishes its intensity. Scattering and absorption take place simultaneously in the layer until finally the remaining attenuated light re-emerges from the entry surface; this light is called diffuse reflectance.³ Diffuse reflectance depends on the particulate nature of the medium² and on the effective depth of penetration to provide a spectrum representative of the entire sample.²³

According to Birth and Hecht,²² diffusely reflected light is attenuated by a factor $10^{-(kl)}$ where k is the volume-averaged absorption constant and l is the mean path length. For a sample whose composition is not identical at each location, scattering has the effect of randomising the light path through the sample, and what emerges appears analytically more homogenous than what actually exists.^{24,25}

The chemical information in the diffusely reflected light is expressed in the absorption constant, K , whereas the particle size information is expressed in the scattering constant, S , both were conceived as properties of the irradiated layer.³ Numerous workers have proposed theories on absorption and scattering in tightly packed particles³ but the theory of Kubelka and Munk²⁶ was the most general and widely validated.³

The Kubelka–Munk (KM) theory²⁶ has three simplifying assumptions: the scattered radiation is

isotropically distributed, the particles in the layer are randomly distributed and very much smaller than the thickness of the layer, and the layer is subject only to diffused reflection. Through these assumptions, the theory derives the relationship,

$$\frac{K}{S} = \frac{(1-R)^2}{2R} = f(R) \quad (1)$$

where $f(R)$ is the KM function, and R is the diffuse reflectance of the sample. Notice that $f(R)$ is a function only of the ratio of the absorption and scattering coefficients (K/S) and not their absolute values. Equation 1 suggests that for a constant coefficient of absorption K , the reflectance R increases as scattering coefficient S increases (i.e. particle size decreases), while R decreases as K increases (i.e. particle size increases) for a constant S . Experimental results deviate significantly from KM theory when $K/S > 0.13$.³ Felder²⁷ derived an equation relating absorption coefficient in transmission K_T to particle diameter for a system of spherical monodisperse particles

$$K_T = -\frac{3\phi(D_m)\ln\left[1 - \frac{D(1-T_d)}{\phi(D_m)}\right]}{2d} \quad (2)$$

where d is the particle diameter, D is packing density of particles, $\phi(D_m)$ is a function of the maximum packing density D_m , and T_d is the transmittance of a single particle. It has been experimentally confirmed that the absorption coefficient in reflection K_R is proportional to the absorption coefficient in transmission K_T .³ Therefore, K_R must be dependent on particle size just as K_T .^{3,28}

Scattering coefficient S is also a function of particle size increasing with particle sizes $d = 1 \mu\text{m}$ in proportion to $1/d$, which compensates for the particle size dependence of K_R .³ Scattering is inversely proportional to the mean path length.²² In equation form the relationships are

$$S \propto \frac{1}{d} \propto \frac{1}{l} \quad (3)$$

From Equations 2 and 3, and since K_R is proportional to K_T , as d increases K_R and S decrease and radiation penetrates deeper into the powder. This increases the path length l that the light travels, thus

increasing absorbance while reducing diffuse reflectance. As d decreases, light encounters more scattering boundaries (S increases) and the depth of penetration of radiation decreases. This decreases the path length l that the light travels, thus reducing the absorbed fraction of radiation and increasing the diffusely-reflected fraction. In simpler terms, grinding absorbing materials cause them to become paler. This can be demonstrated by the white colour produced from fine pulverisation of blue copper sulfate crystals. If the particles in a sample are not all of the same size, scattering produces an averaging effect.²⁴ Dahm and Dahm,²⁹ in relation to their Representative Layer Theory of Diffuse Reflectance, reported that the contribution of a particle of a particular type to the absorption of the sample is approximately weighted in proportion to its volume fraction while its contribution to the reflectance is approximately weighted in proportion to the fraction of cross-sectional area that the particle type makes up in the representative layer. The absorption ($\log 1/R$) of a particular size range in a ground wheat sample was weighted proportional to its mass fraction.³⁰

Factors such as mean particle size, particle size distribution, particle shape, packing density and surface texture presented to the instrument influence the penetration of radiation into the sample and thus the diffuse reflectance from the sample.^{4,7,10} Since the diffusely-reflected light is the sum of the random reflections at the surface and within the sample, the particle size is an integral part of the NIR absorbance values at all wavelengths.³¹

Duyckaerts³² reported a theoretical equation relating absorption intensity and particle size of a material. For a material consisting of cubic particles with quantity sufficient to give n number of layers, the absorption intensity is:

$$A = \log\left(\frac{I_0}{I_t}\right) = -\frac{m}{Psp d} \log[(1-P) + PT_d] \quad (4)$$

where I_0 is the intensity of the incident light, I_t is the intensity of transmitted light, m is the mass of the substance, p is specific weight, s is the surface area of a section of a pellet normal to the beam, d is the cube's edge (particle dimension), P is the fraction of the surface of the beam spot covered by a monolayer of particles (original notation used K which might be

confused with absorption constant) and T_d is the transmittance of one particle (original notation used θ).

When P and T_d are constant, Equation 4 can be simplified as

$$\log\left(\frac{I_0}{I_t}\right) = \frac{K_1}{d} \quad (5)$$

where

$$K_1 = -\frac{m}{P_{sp}} \log[(1-P) + PT_d] \quad (6)$$

K_1 is the slope of the relationship between spectral intensity and the reciprocal of particle dimension ($1/d$) for a particular ground material; it can be obtained empirically. Without quantifying the variables in Equation 6, Otsuka and Matsuda³³ obtained a linear relationship between spectral intensity (based on reflectance) and reciprocal mean particle size of phenytoin (a pharmaceutical product). The relationship of particle size to transmittance (Equation 4) was applicable to diffuse reflectance provided that the penetration depth of the NIR beam was affected considerably by the scattering coefficient.³³

The mean depth of penetration is related to the inverse of absorption coefficient K .² For weak absorbers (small K), light penetrates deeper into the sample and is extensively absorbed. For strong absorbers (large K), a large part of the light will be specularly reflected at the surface. This explains why strongly absorbing materials can absorb very little, whereas weakly-absorbing materials by comparison can absorb a considerable portion of the incident radiation.² The NIR region is used for quantitative measurements of coarsely ground particles because its bands have low absorptivities, which does not cause interferences due to complete absorption (saturation) or specular reflection, typical of the mid-IR.²³ Thus NIR diffuse reflectance can provide the representative composition of whole ground wheat whereas, mid-IR only the surface characteristics of wheat particles.²³ It follows that mid-IR diffuse reflectance of ground wheat has no dependence on particle size because of the low effective depth of penetration. Olinger and Griffiths³⁴ showed that the effective penetration depth of the light beam could only be two to three diameters long for particles of

about 100 μm , especially when the absorption by the surrounding constituents is strong.

Bull³⁵ derived a simplified model of the Kubelka–Munk (KM) equation to evaluate the dependence of NIR reflectance on particle size. The model assumed a material consisting of an infinite series of homogenous, thin (one-dimensional) slabs set perpendicular to incident radiation. Thus the wavelength-dependent scattering and refraction properties of the material can be ignored and only the reflection and transmission at each refractive index discontinuity and the propagation of the unabsorbed fraction of light through the slab are considered. It further assumed that the depth of the slab is $>1/2$ the coherence length of the incident radiation, thus it is possible to add together the components of light which are reflected back out of the slab without considering their relative phases. The total fraction of light reflected back from the infinite series of sheets for normal incidence angle $\theta = 0$ is expressed as

$$\frac{(1-F)^2}{2F} = \frac{A}{R} \quad (7)$$

where A is total absorption and R is the total reflection. Bull³⁵ showed that the model could be used to detect the effect of particle size on reflectance of ground wheat samples for mean particle size of up to at least 350 μm .

Burger *et al.*²⁸ derived an equation of radiative transfer for diffuse reflectance and transmittance by using a three-flux approximation. Using a collimated beam that illuminated the powdered sample and an integrated sphere that measured diffused transmittance and absorbance, the scattering and absorption coefficients of the sample were extracted by the radiative transfer equation. The separated absorption and scattering coefficients provide more information about particle size, agglomeration and chemical composition than only the ratio of these coefficients as in KM function. The scattering effects were then separated from absorption effects before calibration to achieve better linearity. This method was used to analyse the scattering and absorption properties of paracetamol and lactose. In a related study Burger *et al.*³⁶ found that PLS calibrations of diffuse reflectance data of two-component lactose and paracetamol powders pretreated by multiple

scattering correction (MSC) were improved when the scattering coefficient was known. MSC assumes a constant scattering coefficient over a considered wavelength range. Knowing the scattering coefficient, separately from absorption coefficient, enables the calibration to be restricted to the wavelength ranges where MSC assumption is valid.

Dahm and Dahm^{29,37} derived an expression more general than the KM equation using plane parallel mathematics and two-flux approximation. The absorption–remission (or reflectance) function for a material of any thickness is expressed as a function of fractions of incident light absorbed (a), remitted (r) and transmitted (t) by a specified layer.

$$A(r, t) = \frac{[(1-r)^2 - t^2]}{r} = \frac{(2-a-2r)a}{r} \\ = \frac{2a_0}{r_0} = \frac{(1-R)^2}{R} \quad (8)$$

The Dahm equation gives an exact solution for remission from and absorption by any layers whose absorption and scattering properties are fully defined. In the case of infinitesimal particles (very thin layers) with low absorption, it gives results equivalent to the KM equation. However, it is not limited to infinitesimal particles; it is expected to be more useful in evaluating the remission of real systems. To be useful for quantitative analysis, it must be related to measurable properties of a real sample, rather than properties of an arbitrarily defined layer.

Particle size analysis

Reference method and unit

Various methods of particle size analyses measure different physical dimensions, hence the term “particle size” is defined in terms of a measurement technique and a spatial dimension.³⁸ The method is inseparable from the unit. Two of the numerous terms used for particle size and which are relevant to NIR reflectance–particle size applications are volume diameter and sieve diameter.

Methods of particle size measurement can be classified as direct and indirect. Scanning electron microscopy (SEM) and sieving are direct methods.

Indirect techniques measure a property of the particle and then through a calibration calculate the “size.” An example is laser diffraction. Most of the NIR particle size studies used laser diffraction as reference method^{8,16,17,39,40} (Table 1). Laser diffraction reportedly can measure the size range of 0.05–3500 μm within 30 s, based on a recent model with free-fall dry powder feeder.⁴¹ Hareland³⁹ reported that laser diffraction (and percent volume of particles) had better precision than sieving analysis (and percent mass of particles), and thus was a better reference method for flour particle-size distribution. This is understandable because laser diffraction, like NIR reflectance spectroscopy, gives three-dimensional size and shape information. By contrast, sieving, like SEM, gives two-dimensional size information.^{25,33} Also, fine particles had a tendency to stick to the underside of fine sieves thus contributing to error in sieving analysis.³⁹

However, the choice of reference method is determined mainly by the size properties of the particles to be measured and the method to be “replaced” (in an online application) by the NIR reflectance technique. Pasikatan³⁰ used sieving analysis as reference method because the NIR reflectance-based system was intended to give information about the cumulative percent mass of four size fractions of first-break ground wheat, the information useful to flour millers.

Tsuge *et al.*⁴² reported that the overall absorption intensity A_T could be expressed as:

$$A_T = \Sigma(A_d f_v) \quad (9)$$

where A_d is the absorption intensity of particles of a given size or size range and f_v is the volume frequency of particles of that size or size range. Based on this they reasoned that the effect of particles having smaller size than the mean particle diameter was greater than the effect of particles having size larger than the mean particle diameter. This could only be true if the smaller-sized particles are dominant, in terms of volume fraction.²⁹ Pasikatan³⁰ observed that percent mass could be used instead of volume frequency in Equation 9. For first-break ground wheat models based on mass, size ranges having more mass—thus having more contribution to the A_T —were predicted better than those with lesser mass.³⁰

Sampling and sample selection

The main source of error in NIR analyses lies with the samples, their selection, preparation and reference analysis.²⁵ This is true whether the objective is to determine a chemical constituent or the particle size. Williams²⁵ discussed two ways of sample selection: the conventional and the spectral. In conventional sample selection, sufficient samples are selected to obtain a Gaussian distribution with respect to the range of the constituents. For the second method, samples are selected based on spectral characteristics.

For conventional sample selection, within-group models minimise the variance characteristic of across-group models. For example, in NIR protein analysis, the standard deviation for the data for all wheat classes was larger than the standard deviation for the individual classes.⁴³ Because the starch–protein matrix of the wheat endosperm influences fracture behaviour of wheat,⁴⁴ which in turn determines the particle size properties, then the variations in size properties (and thus absorption and scattering) should be narrower for a specific wheat class than for all wheat classes. When samples were grouped according to wheat class, models for estimating the size fractions of first-break ground wheat performed better than models for all wheat classes.³⁰

Method of sample presentation

The method of presenting ground or powdered samples to the NIR spectrometer must ensure that: (1) the layer and surface are representative of the sample's particle-size distribution and physico-chemical properties²⁵ and (2) the layer is presented in a repeatable or reproducible manner.⁴⁵

The non-linearity that occurs in the analysis of NIR spectra of mixtures could be explained by the light not meeting a representative set of particles.³¹ Loading of sample cells is one of the most critical steps in NIR analysis because NIR senses mainly the surface layer²⁵ and factors associated with the sample surface increases the spectral variance.¹⁰ Devaux *et al.*³¹ provided experimental evidence that the particles on the sample surface have more determining effect than those beneath the surface. Using principal component analysis of NIR spectra and images taken from binary mixtures of ground wheat and rapeseed with varying proportions, they identified

three principal components. The first principal component described the scattering effect, the second the proportions of the particles at the sample surface, and the third explained the particles beneath the surface.

The degree of compaction is another factor involved in reproducibility of the sample layer.^{45,46} A certain amount of randomness in the orientation of interfaces and amount of material are essential to bring about complete diffusion of light.²² Equation 2 shows that packing density affects reflectance. Compression of the sample against a flat surface might destroy complete randomness, but the alternative of not packing could leave voids in the sample that could be another source of error.²⁴ Wetzel²⁴ recommended incomplete flattening so that each different particle in the sample would present its own surface to the incident light. The amount of sample, its even distribution and packing density on the sample cell must be maintained.^{17,25,47}

Some NIR reflectance–particle size studies did not describe the method of presenting the ground or powdered samples to the NIR spectrometer.^{16,39,40} For the fine samples used in those studies ($\leq 315 \mu\text{m}$) this was not probably critical and the funnel drop into a standard sample cell would have been adequate to ensure representativity and repeatability of the sample surface and layer presented. Osborne *et al.*⁴⁷ used a pressure pad to maintain packing density of flour samples in a sample holder. Blanco *et al.*⁴⁶ compacted ground piracetam in a sample cell before presentation, but the extent of compaction was not quantified. Ilari *et al.*¹⁵ used a flat device angled at 30° to remove excess sample and tapped the samples 180 times to get compaction. As the particle size of the sample increases spectral reproducibility decreases;⁴⁶ hence the method of presentation becomes critical.

Pasikatan³⁰ developed a method of sample presentation for first-break ground wheat (size range: $<1\text{--}3360 \mu\text{m}$) to ensure spectral repeatability. The method involved dropping a pre-mixed, constant-mass sample from a fixed height into a cylinder with three layers of randomising rods. The degree of compaction was repeatable and the random orientation of the particles in the layer was not disrupted. Sufficient thickness of the layer is also critical to prevent transmission of light and ensure adequate scattering

so that the diffusely-reflected light could carry the complete particle size information of the sample layer.

Spectral data pretreatments

Spectral data pretreatments are used to linearise the data and to correct for scattering effects.⁴⁸ While there is no question about linearising the reflectance spectra by converting these to apparent absorbance, $\log(1/R)$, or Kubelka–Munk (KM) transform, the question is which pretreatment is appropriate for particle size applications—knowing that most of these correct for particle size effects. $\log(1/R)$ linearisation was done in most NIR reflectance–particle size studies (Table 1) as well KM linearisation.^{15,16} Pasikatan³⁰ evaluated the effect of KM and $\log(1/R)$ linearisation on spectral data from first-break ground wheat from six wheat classes. Models were developed using Partial Least Squares for prediction of five size fractions (percent mass for >1041, 375–1041, 240–375, 136–240 and <136 μm size ranges). For the wavelengths used (500–1700 nm), $\log(1/R)$ gave better results than KM models for all size fractions. One probable reason for this result was the NIR reflectance spectrometer did not cover the range 1100–2500 nm, a wavelength region where scattering effects were more pronounced.^{10,18} Another possible explanation was since the matrix surrounding the analyte absorbs radiation at the same wavelength as the analytical band, then deviations from the linearity of the KM function against concentration occurs.³⁴

Some spectral pretreatments used in quantitative chemical applications helped yield good NIR reflectance–particle size models. Mean centring (subtraction of the mean from the individual spectra), a technique that reduced the number of PLS factors in conventional NIR reflectance applications,⁴⁹ also improved the performance of NIR reflectance–particle size models.^{16,50} Mean centring helped eliminate baseline differences caused by variable sample porosity.¹⁶ Hareland³⁹ reported that the second derivative transformation using segment length of 10 data points over which the derivative was taken and 10 data points over which the function was smoothed yielded the best calibration for PLS-based particle size models. First or second derivatives reduce spectral variance caused by particle

size.^{8,10,25} However, when used after unit area normalisation, these yield robust PLS models for particle size.⁵⁰ Unit area normalisation could correct for indeterminate path lengths when there was no means of measuring it. It involved calculating the area under the curve for the entire spectrum.⁵¹ Further studies on pretreatments appropriate for spectral data for NIR–particle size models are needed.

Calibration model selection and validation

Scattering is not a wavelength-independent effect²⁸ but an all-wavelength one^{10,18} Thus full-spectrum NIR reflectance–particle size models, theoretically, should perform better than specific-wavelength models. However, this depends on the size range being estimated. Full-spectrum models based on Partial Least Squares regression performed well when three to five size ranges of particles in a sample were estimated.^{39,50} PLS concentrates the useful spectral information into the first few factors and allows interpretation of the underlying chemical and physical phenomena through spectral loadings and spectral residuals.⁵² For a specific wheat class model (hard red winter), one to three PLS factors accounted for particle size effects,³⁰ which was consistent with previous findings.^{31,52} O'Neil *et al.*¹⁷ used three principal components for predicting 11 size fractions (the entire particle size distribution) of microcrystalline cellulose.

If only one size range is being estimated, e.g. median particle size, two to four wavelengths have been found sufficient for samples with narrow size distribution (Table 1). Osborne *et al.*⁴⁷ used a two-wavelength (1288 and 1720 nm) MLR model to predict wheat kernel texture from wheat flours (percent flour that passed through a 76 μm air-jet sieve). Blanco *et al.*⁴⁶ used a two-wavelength MLR model to determine the mean particle size of piracetam: the wavelength of maximum correlation (1818 nm) corresponding to a minimum in the absorption band (1930 nm) which ensured minimal dependence on chemical absorption. The results were comparable to a three-factor PLS model. Rantannen and Yliruusi⁵³ continuously measured four wavelengths (1740, 1835, 1990 and 2145 nm): 1740 nm was used for correction of background level and 2145 as particle size measurement wavelength. The baseline-cor-

Table 1. Summary of NIR reflectance–particle size studies.

Powdered material	Particle property/size range (μm)	Reference method	Model and wavelengths used	Reference
Wheat flour	Air-jet sieve (AJS) value (<76)	AJS	MLR ^a (1288, 1720 nm)	47
Aspirin, ascorbic acid, ammonium phosphate dibasic-aluminium oxide	Reciprocal of particle size; 62–247, 139–222, 40–140, 62–111	LD ^b	Log $1/R$ vs $1/d$ (selected; from 1800 to 2500 nm)	8
NaCl, broken glass, sorbitol	Mean particle size; 0–200, 0–200, 0–315	Sieving	Log $1/R$ and KM ^c (1100–2500 nm)	15
Pea flour	Mean particle diameter, 13 size fractions, 89–1414	—	PCA ^d (1100–2500 nm)	18
Piracetam (drug)	Mean particle size; range: ~200–350	Sieving	PLS ^e and MLR (1100–2500 nm)	46
Wheat flour (except durum wheat)	3 size fractions: <10 , 10–41, 41–300	LD	2 nd der. (400–2500 nm)	39
Micronised active compound in a lactose monohydrate (LMH) matrix	Mass median particle size; 8–20	LD	PCA (1100–2500 nm)	40
Aspirin, anhydrous caffeine, paracetamol, microcrystalline cellulose (MC)	Median particle size (d_{50}); 19.2–183 (LMH), 24–406 (MC) ^g	LD and sieving	MLR and KM (1000–2500 nm)	16
Microcrystalline cellulose	Median particle size, 75–186.5	LD	1740, 1835, 1990, 2145 nm	53
Microcrystalline cellulose	11 quantiles ($d_5, d_{10}, \dots, d_{90}, d_{95}$)	LD	MLR and PCR	17
First-break ground wheat	Percent mass of size fractions (>1041 , 375–1041, 240–375, 136–240, <136 or >375 , >240 , >136)	Sieving analysis	PLS; 600–1700 nm	30, 50

^aMultiple linear regression^bLD = laser diffraction^cKubelka–Munk model^dPrincipal component analysis^ePartial Least Squares regression

rected absorbance yielded a high correlation ($r^2 = 0.96$) with median particle size. O'Neil *et al.*¹⁶ used single wavenumber quadratic least squares regression and two-wavenumber MLR calibrations for NIR reflectance, mean-corrected reflectance, absorbance and Kubelka–Munk function against median particle size (d_{50}), reciprocal d_{50} and $\ln(d_{50})$. The best calibrations ($r = 0.99$) were obtained using reflectance data against $\ln(d_{50})$ for microcrystalline cellulose and lactose monohydrate sieve fractions.

Statistics typically used to assess the goodness of a calibration model for chemical applications of NIR reflectance are also applicable for particle size. These include correlation coefficient (r), coefficient of determination (r^2), standard error of cross-validation (*SECV*), standard error of prediction (*SEP*), mean and standard deviation of measured and predicted values and coefficient of variability (ratio of *SEP* to the mean of reference values). Williams⁹ reported the definitions and applications of these terms. *RPD* (ratio of *SEP* to standard deviation) and *RER* (ratio of *SEP* to range of reference data) were also proposed by Williams⁵⁴ for comparison of size fractions across studies.

Applications

Possibly the earliest NIR reflectance–particle size study was done by Osborne *et al.*⁴⁷ (Table 1). Although they related wheat grain kernel texture (hardness) to NIR reflectance, the measure of texture was the percent of 10 g flour that passed through a 76 μm air-jet sieve in 1 min—a size fraction of flour. Reflectance values (1100–2500 nm) were smoothed and compressed before wavelength search was done by MLR. The best correlation of NIR reflectance ($\log 1/R$) with air-jet set values, thus hardness, were obtained with 1288 and 1720 nm ($r = 0.99$).

Ciurczak *et al.*⁸ determined the mean particle size of pure pharmaceutical products (aspirin, ascorbic acid, aluminium oxide, ammonium phosphate dibasic) using NIR reflectance spectroscopy (Table 1). The reciprocal of mean particle size ($1/d$) was plotted against absorbance $\log (1/R)$ for selected wavelengths and they found a steep inversely linear relationship for $d > 200 \mu\text{m}$ down to about 85 μm followed by a less steep line for $d \leq 85 \mu\text{m}$. They pro-

posed that the rapidly diminishing absorbance line is controlled almost entirely by the S coefficient of the KM equation while K exerted a larger influence on particles $\leq 85 \mu\text{m}$. Their results showed that the measurement of particle size of pure materials could be done most accurately over the $>85 \mu\text{m}$ size range and grinding to $\leq 85 \mu\text{m}$ would greatly reduce particle size effects. They further showed that the absorbance values at 1658 nm (major peak) against the absorbance values at 1784 nm (baseline) was linear for different size particles of aspirin. The technique was valid for ratios of any two wavelengths. NIR reflectance spectroscopy has been used to measure median particle size (d_{50}) of a number of powdered drugs and pharmaceutical excipients¹⁶ and to measure the particle size of one powdered material in the presence of another powdered material, with little or no sample preparation⁴⁰ (Table 1). A technique based on NIR reflectance spectroscopy was developed for online determination and control of particle growth during granulation⁵³ (Table 1).

Ilari *et al.*¹⁵ determined the mean particle size of three different types of chemically simple powders (glass beads, sodium chloride and sorbitol) (Table 1). The reflectance spectra were linearised using $\log (1/R)$ and the Kubelka–Munk transform, K/S . In order to separate the absorption K from the multiplicative scattering effects ($1/S$) in the NIR data, each spectrum was subjected to the multiple scattering correction technique. Mean particle size could be determined from linearised and multiple scattering-corrected NIR reflectance data for a given type of powder. Up to 99% of the particle size variance was explained by the regression. Chapelle *et al.*¹⁸ studied the use of NIR reflectance spectroscopy for particle size analysis of pea flour. Smooth peas were shelled, ground and sieved to 13 different fractions graded by particle size (80 to 1250 μm) (Table 1). The size fractions were either analysed directly or were recombined to produce synthetic samples of defined particle size characteristics. Using Principal Component Analysis they found that NIR spectroscopy could be used to classify unknown samples according to particle size characteristics without reference to chemical data. Principal components of absorbances related primarily to mean particle diameter, for both pure particle fractions and recombined samples.

Blanco *et al.*⁴⁶ determined the mean particle size of different batches of piracetam (a neuro-physiological drug) and quantified this compound in a pharmaceutical preparation using NIR reflectance spectroscopy (Table 1). Particle size was determined using a three-factor PLS model using the wavelength range 1300–2500 nm. Piracetam in the preparation was determined using a five-factor PLS model of the second derivative spectra. The prediction errors were 15 μm and 6.1 mg (equivalent to 3% of piracetam content in the commercial dosage), respectively. This study showed the potential of NIR spectrometers for two-in-one sensing (sensing of chemical constituents as well as particle size of the powder sample).

Hareland³⁹ predicted the percent volume of wheat flour particles of three size ranges (<10 μm , 10–41 μm and 41–300 μm) to within two standard deviation for 96% of the samples tested using NIR reflectance spectroscopy. He obtained standard errors of cross-validation of 0.26, 0.87 and 1.11, and standard errors of prediction of 0.35, 1.17 and 1.13 for the three size ranges, respectively (Table 1). O'Neil *et al.*¹⁷ used three-wavelength MLR model and three-component PCR (4008–9996 cm^{-1} or 1000–2495 nm) models to predict the cumulative particle size distribution of microcrystalline cellulose (11 size fractions: 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95%; size range: 6.45–546.76 μm) from forward angle laser light scattering measurements. Both MLR and PCR models predicted well the 11 size fractions but the PCR model was computationally faster and slightly more robust. Using offline methods, Pasikatan *et al.*⁵⁰ evaluated NIR reflectance spectroscopy as a granulation sensor for first-break ground wheat, a coarsely ground product. The objective was to use NIR reflectance as a basis for online control of a roller mill's roll gap.

Summary

NIR reflectance is influenced by the particle size properties of ground or powdered materials. Thus using proper procedures and calibration, NIR reflectance spectroscopy can be used for particle size analysis. The effects of particle size, distribution, surface texture and compaction are expressed

in a sample's scattering constant. Scattering effect is expressed in all NIR wavelengths. However, a sample's absorption constant is not entirely free from particle size effects. The contribution of a size range to the absorption of a powder sample is approximately weighted in terms of its volume or mass fraction. Hence, size ranges with more amounts in a powder mixture tend to be predicted better than size ranges with lesser amounts. Sample selection methods that reduce the variance of the spectra should be used. As in any quantitative NIR reflectance analysis, the sample presented must be representative of the whole and the amount, surface and layer characteristics and degree of compaction must be repeatable for each presentation. Spectral pretreatments that reduce particle size effect should be evaluated first for this application. For finely-ground samples, derivatisation of the spectra was shown to work well. For coarser ground samples, pretreatments that corrected for indeterminate path lengths yielded models that have good predictive ability. Single- and double-wavelength models have been shown to work for determining a single size property, such as mean particle size, whereas full-spectrum models (MLR, PLS or PCR) were appropriate for determining three to 11 size ranges.

Most of the studies cited in this review are in the pharmaceutical industry where the control of particle size of drugs and the amount of active ingredients in a mixture are critical. However, studies in estimating the size distribution of wheat flour, pea flour and ground wheat indicate strongly the feasibility of using NIR reflectance for real-time monitoring and even controlling of the size reduction process of these products. In these applications, NIR reflectance has the advantages of speed, simplicity, low-operating cost and a two-in-one sensor.

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